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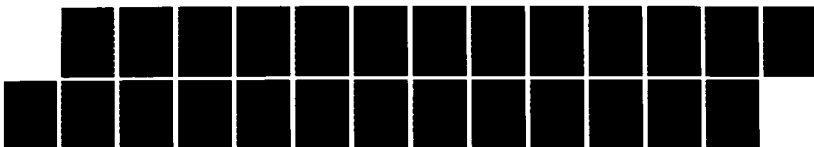
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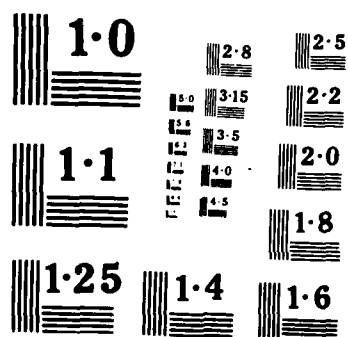
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TECHNICAL REPORT No. 8

Photodissociation of Molecules at Structured Metallic Surfaces

by

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Prepared for Publication

in

Journal of Chemical Physics

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June 1986

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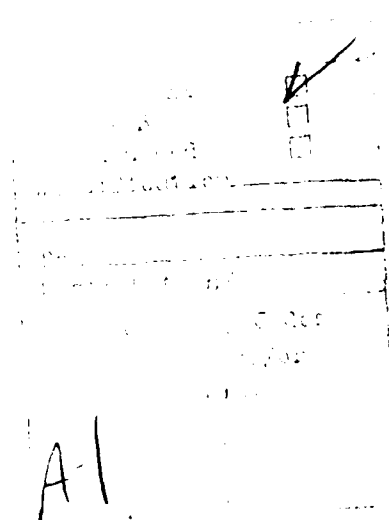
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2a. SECURITY CLASSIFICATION AUTHORITY		3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution unlimited													
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE															
4. PERFORMING ORGANIZATION REPORT NUMBER(S) UBUFFALO/DC/86/TR-8 ✓		5. MONITORING ORGANIZATION REPORT NUMBER(S)													
6a. NAME OF PERFORMING ORGANIZATION Depts. Chemistry & Physics State University of New York		6b. OFFICE SYMBOL (If applicable)													
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6c. ADDRESS (City, State and ZIP Code) Fronczak Hall, Amherst Campus Buffalo, New York 14260		7b. ADDRESS (City, State and ZIP Code) Chemistry Program 800 N. Quincy Street Arlington, Virginia 22217													
8a. NAME OF FUNDING/SPONSORING ORGANIZATION Office of Naval Research		8b. OFFICE SYMBOL (If applicable)													
9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER Contract N00014-86-K-0043															
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13a. TYPE OF REPORT Interim Technical		13b. TIME COVERED FROM _____ TO _____													
14. DATE OF REPORT (Yr., Mo., Day) June 1986		15. PAGE COUNT 18													
16. SUPPLEMENTARY NOTATION Prepared for publication in the Journal of Chemical Physics															
17. COSATI CODES <table border="1"><tr><td>FIELD</td><td>GROUP</td><td>SUB. GR.</td></tr><tr><td></td><td></td><td></td></tr><tr><td></td><td></td><td></td></tr><tr><td></td><td></td><td></td></tr></table>		FIELD	GROUP	SUB. GR.										18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) MOLECULAR DISSOCIATION STRUCTURED METALLIC SURFACES OPTIMAL AND CRITICAL DISTANCES LINE SHAPE SINUSOIDAL GRATING I <sub>2</sub> ON SILVER	
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22a. NAME OF RESPONSIBLE INDIVIDUAL Dr. David L. Nelson		22b. TELEPHONE NUMBER (Include Area Code) (202) 696-4410													
		22c. OFFICE SYMBOL													

PHOTODISSOCIATION OF MOLECULES AT STRUCTURED METALLIC SURFACES

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Abstract

Direct photodissociation of molecules at structured metallic surfaces is considered, where the concepts of optimal and critical distances are introduced into the description of this phenomenon. Numerical results for the distortion of the line shape and the enhancement ratio are obtained for a shallow sinusoidal grating.



## I. Introduction

Ever since the first observation of surface-enhanced Raman scattering (SERS),<sup>1</sup> possible surface enhancement of other optical processes such as resonance fluorescence and photon trapping has been a subject of much interest.<sup>2-6</sup> The related dynamical process of the photodissociation of gas molecules near or physisorbed on a rough metallic surface is also of great interest for the following reasons. From a practical viewpoint, it is the first step that one must study in order to understand and control the various phenomena ranging from the deposition of molecules<sup>7</sup> to heterogeneous catalysis<sup>8</sup> on a rough surface. It is also of great theoretical interest, for although it is now clear that the surface definitely plays a role in enhancing the Raman scattering signal via its plasmon field set up by the laser under resonance conditions,<sup>9</sup> it is not so clear in the case of dissociation. The reason for this is that while the surface plasmon field still enhances the absorption process, line-broadening effects<sup>10</sup> due to transitions to final continuum states play a competing role to suppress the dissociation. These two competing mechanisms, namely, the enhanced local field and the increased decay rate near a structured surface, have also been noticed in the literature.<sup>4,11</sup>

The excitement of this subject is further aroused when we consider that while a model calculation<sup>4</sup> for a molecular dipole adsorbed on a silver sphere shows enhancement effects (although to a much less extent as compared to SERS), a recent experiment<sup>11</sup> on the photochemical degradation of rhodamine 6G adsorbed on a silver-island surface shows no enhancement effect whatsoever, and in some cases even diminution effects are observed. On the other hand, enhanced photodissociation of surface-supported organometallic molecules has been reported.<sup>12</sup> Furthermore, the observation of different

gas/surface dissociation ratios for different metal-alkyl compound induced by UV laser radiation<sup>13</sup> suggests the possible existence of an optimal molecule-surface distance (to be determined by the aforementioned competing mechanisms) at which the dissociation rate is the largest. Based on all the observations mentioned above, we recognize that there are various issues in the photodissociation of molecules at a surface which are still not fully resolved.

In this paper, we present a systematic study of such processes within a simple model. We shall assume our surface to be a shallow sinusoidal grating, bearing in mind that a general structured surface can be viewed as a superposition of many different sinusoidal structures via Fourier analysis. The surface fields for this case are well known,<sup>14,15</sup> and we shall derive an expression for the molecular decay rate on such a surface. We shall see that, with the introduction of such concepts as critical and optimal distances, many of the experimental observations mentioned above<sup>11-13</sup> can be understood (at least qualitatively) from this simple approach.

## II. Cross Section

Within first-order time-dependent perturbation theory, the quantum-mechanical cross section for a dipole transition can be expressed in proportion to the line-shape function  $I(\omega)$  as<sup>16</sup>

$$\sigma(\omega) = A_0 I(\omega) \quad , \quad (1)$$

where  $A_0$  is the proportionality constant, and  $I(\omega)$  is given by the Fourier transform of the autocorrelation function

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt \langle \vec{\mu}^*(0) \cdot \vec{\mu}(t) \rangle e^{-i\omega t} \quad , \quad (2)$$

where  $\vec{\mu}(t)$  is the Heisenberg time-dependent operator for the induced dipole moment of the molecule. Instead of solving the problem in a fully quantum-mechanical way, we adopt a semiclassical approach by describing  $\vec{\mu}(t)$  in the context of the classical mechanical model for a damped harmonic oscillator. Corrections of higher order in Planck's constant can in principle be sought by following the formalism of Ref. 16. Thus we have<sup>4</sup>

$$\ddot{\vec{\mu}}(t) + (\omega_M^0)^2 \vec{\mu}(t) + \gamma_M^0 \dot{\vec{\mu}}(t) = (\omega_M^0)^2 \alpha_M \vec{E} \quad (3)$$

where  $\omega_M^0$  and  $\gamma_M^0$  are respectively the molecular frequency and decay rate in the bulk,  $\alpha_M$  is the molecular polarizability, and  $\vec{E}$  is the external field at the site of the molecule.

For a molecule sitting on a metallic surface, the total external field can be written in the form

$$\vec{E} = \vec{E}_0 + \vec{E}_r + \vec{E}_{sp} + \vec{E}_{im} \quad (4)$$

which represents the sum of the incident, reflected, surface plasmon and image fields. If we Fourier analyze Eq. (3) and assume that  $\vec{E}(\omega)$  can be written in the form<sup>4</sup>

$$\vec{E}(\omega) = [1 + A(\omega)] \cdot \vec{E}_0(\omega) + G(\omega) \cdot \vec{\mu}(\omega) \quad (5)$$

where all the coefficients are in general tensors, we can write the solution of Eq. (3) in the form<sup>4</sup>

$$\mu(t) = \mu(\omega) e^{-i\omega t} \quad (6)$$

with

$$\mu(\omega) = \frac{\alpha_M (\omega_M^0)^2}{\omega_M^2 - \omega^2 - i\omega\gamma_M} \hat{n}_\mu \cdot [1 + A] \cdot \vec{E}_0 \quad (7)$$



Here  $\hat{n}_\mu$  is the unit vector of the direction of the molecular dipole,  $\omega_M$  and  $\gamma_M$  are respectively the "surface modified" molecular frequency and decay rate which are to be determined by the image field  $G(\omega) \cdot \vec{\mu}(\omega)$  in Eq. (5),<sup>4</sup> and we have assumed a monochromatic incident field of the form  $\vec{E}_0 = \vec{E}_0 e^{-i\omega t}$ . By substituting Eqs. (6) and (7) into Eqs. (1) and (2), we obtain the cross section in the form

$$\sigma(\omega) = 2\pi c \alpha^2 a_0 |\hat{n}_\mu \cdot [1 + A] \cdot \hat{n}_0|^2 \frac{\gamma_M}{(\omega - \omega_M)^2 + (\frac{\gamma_M}{2})^2}, \quad (8)$$

where  $\hat{n}_0 = \vec{E}_0 / E_0$ ,  $c$  is the speed of light,  $\alpha$  the fine structure constant and  $a_0$  the Bohr radius. It turns out that this semiclassical approach leads to the same result as the one obtained from a complete classical treatment by calculating the Poynting fluxes of the incident beam and of that adsorbed by the molecular system.<sup>4</sup> We also note that Eq. (8) exhibits the general Lorentzian form which is appropriate for adsorption as well as for fast (direct) dissociation processes,<sup>16</sup> for the latter takes place on a time scale on the order of  $10^{-14}$  s following the absorption, which leads to a yield of almost unity for such reactive processes.<sup>17</sup>

### III. Surface Field

It is clear from Eq. (8) that the effects of the surface enter into the process through the terms  $A$ ,  $\gamma_M$  and  $\omega_M$ . Since under most circumstances, the change of the molecular frequency due to the presence of the image field is almost completely negligible,<sup>10</sup> we shall assume  $\omega_M \approx \omega_M^0$  in all our calculations below. To investigate the surface effects on  $A$  and  $\gamma_M$ , we shall consider a simple geometrical setting of the problem. Specifically, we shall consider dissociation on a shallow sinusoidal metallic grating with

the molecular dipole oriented perpendicular to it along the  $z$ -axis and located at  $(0,0,d)$ . Furthermore, we shall consider monochromatic  $P$ -polarized incident laser light at an angle of incidence equal to  $\theta$  (see Fig. 1). The surface fields are well known for this case, and following the notations of Ref. 15 (except that we have light incident from the  $z > 0$  region), we can write  $A$  in the form<sup>14,15</sup>

$$A(\omega) = \begin{pmatrix} 0 & -\frac{k_z}{k_t} \operatorname{Re} \frac{2iK_z d}{k_t} + \frac{i\Gamma_g}{k_g} \operatorname{Se}^{(ik_z - \Gamma_g)d} \\ 0 & \operatorname{Re} \frac{2ik_z d}{k_t} + \operatorname{Se}^{(ik_z - \Gamma_g)d} \end{pmatrix}, \quad (9)$$

where  $K_g = \frac{\omega}{c} \sin \theta + g$ ,  $g = 2\pi/\lambda_g$  with  $\lambda_g$  being the spatial period of the grating,  $\Gamma_g = (K_g^2 - \omega^2/c^2)^{1/2}$ ,  $k_z = \frac{\omega}{c} \cos \theta$ ,  $k_t = \frac{\omega}{c} \sin \theta$ , and  $\theta$  is the angle of incidence. The quantities  $R$  and  $S$  in Eq. (9), originating respectively from the reflected and surface plasmon fields, are given as

$$R = \frac{\epsilon k_z - i\beta}{\epsilon k_z + i\beta} \quad (10)$$

$$S = \frac{2(\xi_g K_g) k_z \beta (1-\epsilon)}{k_t (\epsilon \Gamma_g + \beta_g)} \cdot \frac{\beta \beta_g + \epsilon k_t K_g}{\beta_g (\epsilon k_z + i\beta)}, \quad (11)$$

where  $\beta^2 = k_t^2 - \frac{\omega^2}{c^2} \epsilon$ ,  $\beta_g^2 = K_g^2 - \frac{\omega^2}{c^2} \epsilon$ ,  $\xi_g$  is the amplitude of the sinusoidal grating, and  $\epsilon = \epsilon_1 + i\epsilon_2$  is the frequency-dependent complex dielectric constant of the metallic grating. The plasmon resonance condition is achieved when

$$\frac{\omega^2}{c^2} \epsilon_1(\omega) - K_g^2 [\epsilon_1(\omega) + 1] = 0. \quad (12)$$

In writing  $A(\omega)$  as in Eq. (9), we have assumed a column-vector notation for

any field  $\vec{E}$  in the form  $\begin{pmatrix} E_{\parallel} \\ E_z \end{pmatrix}$ , where  $E_{\parallel}$  is the component on the xy-plane and  $E_z$  is the z-component. Thus, for the perpendicular dipole at (0,0,d),  $\hat{n}_{\mu} = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$  in Eq. (8) and hence we have

$$|\hat{n}_{\mu} \cdot [1 + A] \cdot \hat{n}_0|^2 = |1 + \text{Re} \frac{2ik_z d}{z} + \text{Se}^{\frac{(ik_z - \Gamma) d}{g}}|^2 \sin^2 \theta \quad (13)$$

#### IV. Decay Rate

In order to see completely how the effects of the surface enter into Eq. (8), we now derive an expression for  $\gamma_M$  for a molecule sitting on a shallow sinusoidal grating. For the case of a randomly rough surface, the molecular decay rate has been derived<sup>18</sup> by application of the Rahman-Maradudin formalism<sup>19</sup> for the image potential due to a point charge (e) resting on such a surface. Furthermore, the image potential for a shallow sinusoidal grating has also been worked out by Rahman and Mills<sup>20</sup> following the Rahman-Maradudin formalism. To first order in  $\xi_g/\lambda_g$ , the result can be expressed as

$$\phi(z) = -\frac{e}{8} \frac{(\epsilon-1)}{(\epsilon+1)^2} \xi_g g \{ (\epsilon-1) [gK_0(gz) + \frac{2}{z} K_1(g,z)] + \frac{4K_1(gz)}{z} \} \quad (14)$$

where  $K_0$  and  $K_1$  are the modified Bessel functions. From this, it is straightforward to calculate the image field,

$$\begin{aligned} E(z) = & -\frac{e}{8} \frac{(\epsilon-1)}{(\epsilon+1)^2} \xi_g g \{ (\epsilon-1) [ (g^2 + \frac{4}{z^2}) K_1(gz) + \frac{2g}{z} K_0(gz) ] \\ & + 4 [ \frac{g}{z} K_0(gz) + \frac{2}{z^2} K_1(gz) ] \} \quad (15) \end{aligned}$$

From Eq. (15) and by making use of the properties of  $K_0$  and  $K_1$ , it is not difficult to derive the image field due to a dipole ( $E_{\mu}$ ) on a surface. For a perpendicular dipole located at (0,0,d), we obtain

$$G^R(\omega) \equiv \frac{E_\mu}{\mu} = \frac{1}{8} \frac{(\epsilon-1)}{(\epsilon+1)^2} \xi_g g \left\{ g[(\epsilon-1)(g + \frac{2}{d}) + \frac{4}{d}] (gK_1 + \frac{K_0}{d}) + \frac{4}{d^2} (\epsilon+1) (gK_0 + \frac{3K_1}{d}) \right\} , \quad (16)$$

where  $\mu$  is the dipole moment. Note that this result is first order in  $\xi_g g$ , in contrast to that for a randomly rough surface which has a lowest-order result in  $(\xi_g g)^2$ .<sup>18</sup> Following similar procedures as in Refs. 10 and 18, we obtain

$$\frac{\gamma_M}{\gamma_M^0} = 1 + \frac{3}{2} \frac{q}{k^3} \text{Im} G^F (1 + \frac{\text{Im} G^R}{\text{Im} G^F}) , \quad (17)$$

where  $q$  is the quantum yield of emitting state and  $G^F(\omega)$  is the corresponding function as in Eq. (16) for a flat surface. According to the classical model of Sommerfeld for a perpendicular dipole at  $(0,0,d)$ ,  $G^F$  is given by<sup>10</sup>

$$G^F(\omega) = -k^3 \int_0^\infty du \mathcal{R} e^{-2\ell_1 d} \frac{u^3}{\ell_1} . \quad (18)$$

where  $d = kd$ ,  $\mathcal{R} = \frac{\ell_2 - \epsilon \ell_1}{\ell_2 + \epsilon \ell_1}$ ,  $\ell_1 = -i(1 - u^2)^{1/2}$  and  $\ell_2 = -i(\epsilon - u^2)^{1/2}$ .

Substituting Eqs. (16) and (18) into Eq. (17) and assuming a quantum yield of approximate unity,<sup>10</sup> we can have an accurate estimate of  $\gamma_M$ , and together with the result in Eq. (13), we can investigate the complete surface effects on molecular dissociations via Eq. (8).

## V. Numerical Results and Discussion

To illustrate the surface effects, we consider here the direct dissociation of  $I_2$  molecules at 4500 Å on a silver (Ag) grating. We assume a grating period ( $\lambda_g$ ) of 8000 Å and the ratio  $\xi_g/\lambda_g = 8 \times 10^{-3}$ .

Furthermore, the angle of incidence ( $\theta$ ) is fixed at  $34.4^\circ$  and the components of the complex dielectric constant for Ag are taken from the data compiled by Johnson and Christy.<sup>21</sup> In order to have a more fine adjustment within the neighborhood of resonance frequencies (for both molecular and plasmon resonances), we have numerically fitted the data to obtain the following empirical formulas for  $\epsilon_1$  and  $\epsilon_2$ :

$$\epsilon_1 = -79.80/E_Y^2 - 6.888/E_Y + 6.084, \quad E_Y < 3.12 \text{ eV} \quad (19)$$

$$\epsilon_2 = \begin{aligned} & (1 - 3.704) \ln E_Y (2.466/E_Y^2 + 0.220/E_Y - 0.192)^{1/2}, \quad E_Y < 1.14 \text{ eV} \\ & 0.1(79.70/E_Y^2 + 7.123/E_Y - 6.194)^{1/2}, \quad 1.14 \text{ eV} < E_Y < 3.12 \text{ eV} \end{aligned} \quad (20)$$

where  $E_Y$  is the energy of the incident photon. With all these data fixed, we find from Eq. (12) that the plasmon resonance occurs at a frequency with  $E_Y \approx 2.895 \text{ eV}$ .

Figure 2 shows how the Lorentzian line shape for a free molecule is distorted due to the surface effects. It is of interest to compare these results with those obtained for a molecular dipole located on top of a silver sphere.<sup>4</sup> Since we have adjusted the two resonance frequencies to be almost the same, the "double peak" feature is not observed in our result. We notice further that enhanced dissociation is obtained as long as the molecule is not too close to the surface. We also find that the line shape becomes highly asymmetric because of surface effects. There seems to exist a window for the plasmon resonance effects at the steep edge of the profile, which is also a property possessed by the famous asymmetric Fano profile.<sup>22</sup> When one goes off resonance to the right, the plasmon field becomes so small that only the incident and reflected fields will predominate the process giving rise to interference phenomenon. Furthermore, if the molecule is too close to the surface (e.g.,  $d = 10 \text{ \AA}$ ), complete diminution will occur. This

gives hint to the existence of a critical distance ( $d_{cr}$ ) below which one does not have any enhancement. In Fig. 3, we plot the enhancement ratio  $\sigma/\sigma_0$  where  $\sigma_0$  is the cross section for a free molecule versus the molecule-surface distance for different fixed laser frequencies. The graphs indeed show the existence of the critical distances as well as the optimal distances ( $d_{op}$ , at which dissociation is a maximum) for each case. More precise numerical results are listed in Table 1.

With the existence of these distances, the experimental observations by Garoff et al.<sup>11</sup> and Ehrlich and Osgood<sup>13</sup> can at least be understood qualitatively. In particular, we observe from graph (a) in Fig. 3 that at the plasmon resonance one can still have a large enhancement in the cross section even at distances far from the surface. This might be the crucial justification for the observation of Ehrlich and Osgood,<sup>13</sup> who found that an appreciable amount of molecular dissociation occurs already in the gas phase far above the substrate for  $Cd(CH_3)_2$  but not for  $Al_2(CH_3)_6$ . For the latter, which is not on plasmon resonance under their experimental conditions, dissociation occurs mostly inside the adlayers.

As a final comment, although we have assumed a perpendicular dipole in our model calculation, we expect that the qualitative features of the results obtained here will prevail if one assumes a parallel or even randomly-oriented dipole. Especially at small molecule-surface distances, the induced decay rate for both the perpendicular and the parallel orientations will be very similar.<sup>10</sup>

#### IV. Conclusions

Within a simple model, we have seen how various experimental observations of photodissociation of molecules on a surface can be understood qualitatively. Furthermore, the concept of critical distance may lead to practical applications. As an example, we suggest that if one could coat the metallic surface by means of the "fatty acid monolayer assembly technique",<sup>23</sup> one could then guarantee that surface-assisted dissociation is maintained and thus achieve a more efficient heterogeneous catalysis process on the surface.<sup>8</sup> To acquire more realistic values for both  $d_{cr}$  and  $d_{op}$ , one can extend the present calculations to cases with deeper gratings. The surface fields in this case have been established in the literature.<sup>24-26</sup> Furthermore, larger roughness requires a reformulation of the treatment of the molecular decay rate, which is possible by incorporating terms of higher order in  $\xi_g$  in Eq. (14) within the Rahman-Maradudin formalism.<sup>19</sup> Work in this direction is in progress in our laboratory.

#### Acknowledgments

One of us (P. T. L.) wishes to acknowledge the considerable help from his colleagues Daniel A. Jelski and Keith Wong. Useful conversations with Youqi Wang and other members in the research group are also gratefully acknowledged. This research was supported by the Air Force Office of Scientific Research (AFSC), United States Air Force, under Contract F49620-86-C-0009, the Office of Naval Research, and the National Science Foundation under Grant CHE-8519053. The United States Government is authorized to reproduce and distribute reprints notwithstanding any copyright notation hereon.

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Table 1. Numerical Results From Figure 3

Graph	Energy of incident photon ( $E_Y$ )	Critical distance ( $d_{cr}$ )	Optimal Distance ( $d_{op}$ )
(a)	2.895 eV	33 Å	340 Å
(b)	2.5 eV	70 Å	210 Å
(c)	2.755 eV	120 Å	280 Å

Figure Captions

1. Geometrical arrangement of the photodissociation process.
2. Distortion of the Lorentzian line profile for various molecule-surface distances for a perpendicular molecular dipole. The system consists of an  $I_2$  molecule on a silver sinusoidal grating. Refer to the text for numerical data.
3. Enhancement factor vs. molecule-surface distance for various incident laser frequencies. (a)  $E_Y = 2.895$  eV (at plasmon resonance), (b)  $E_Y = 2.5$  eV and (c)  $E_Y = 2.755$  eV (at molecular resonance). Other parameters are the same as in Fig. 1.

Figure 1

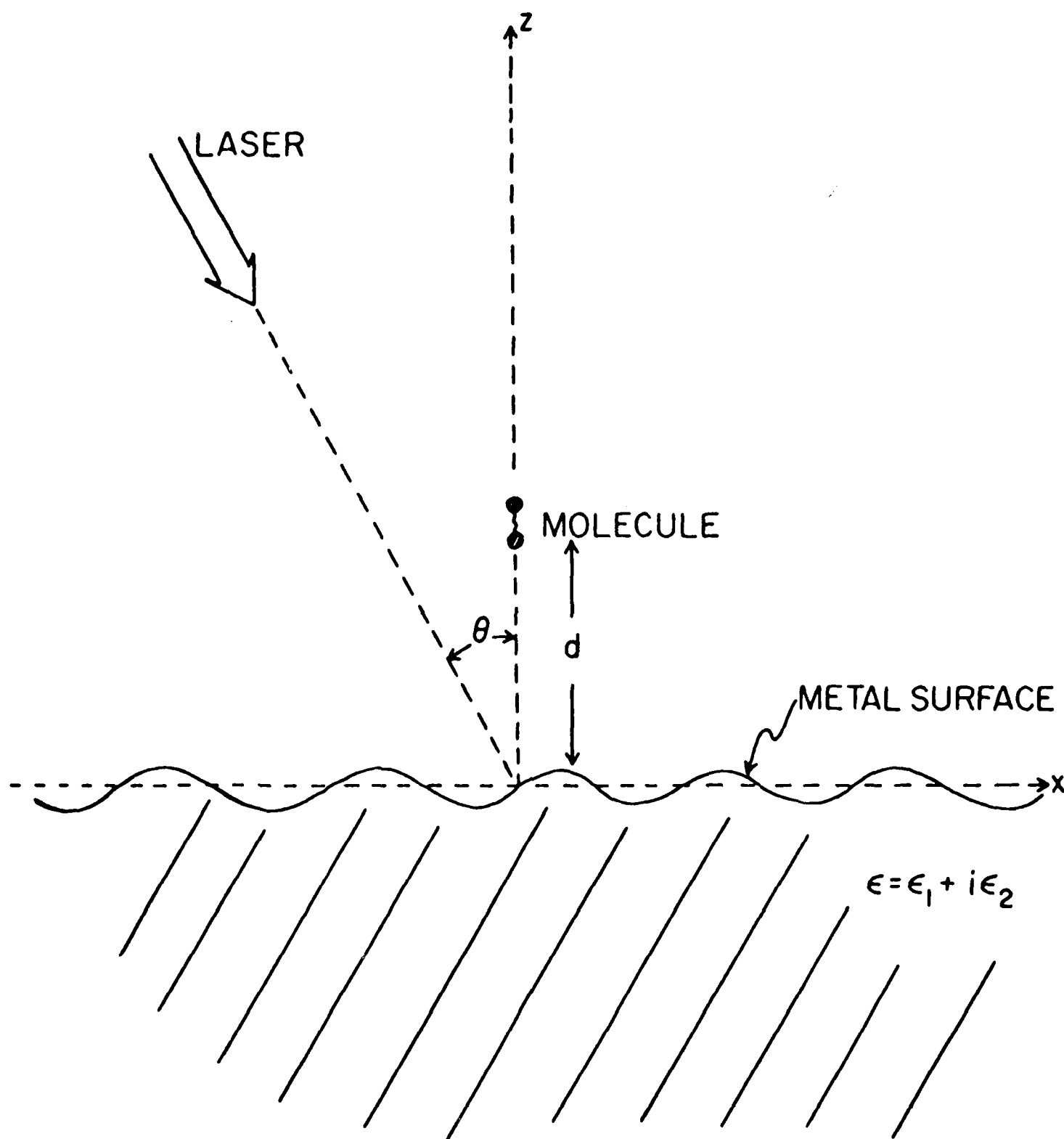


Figure 2

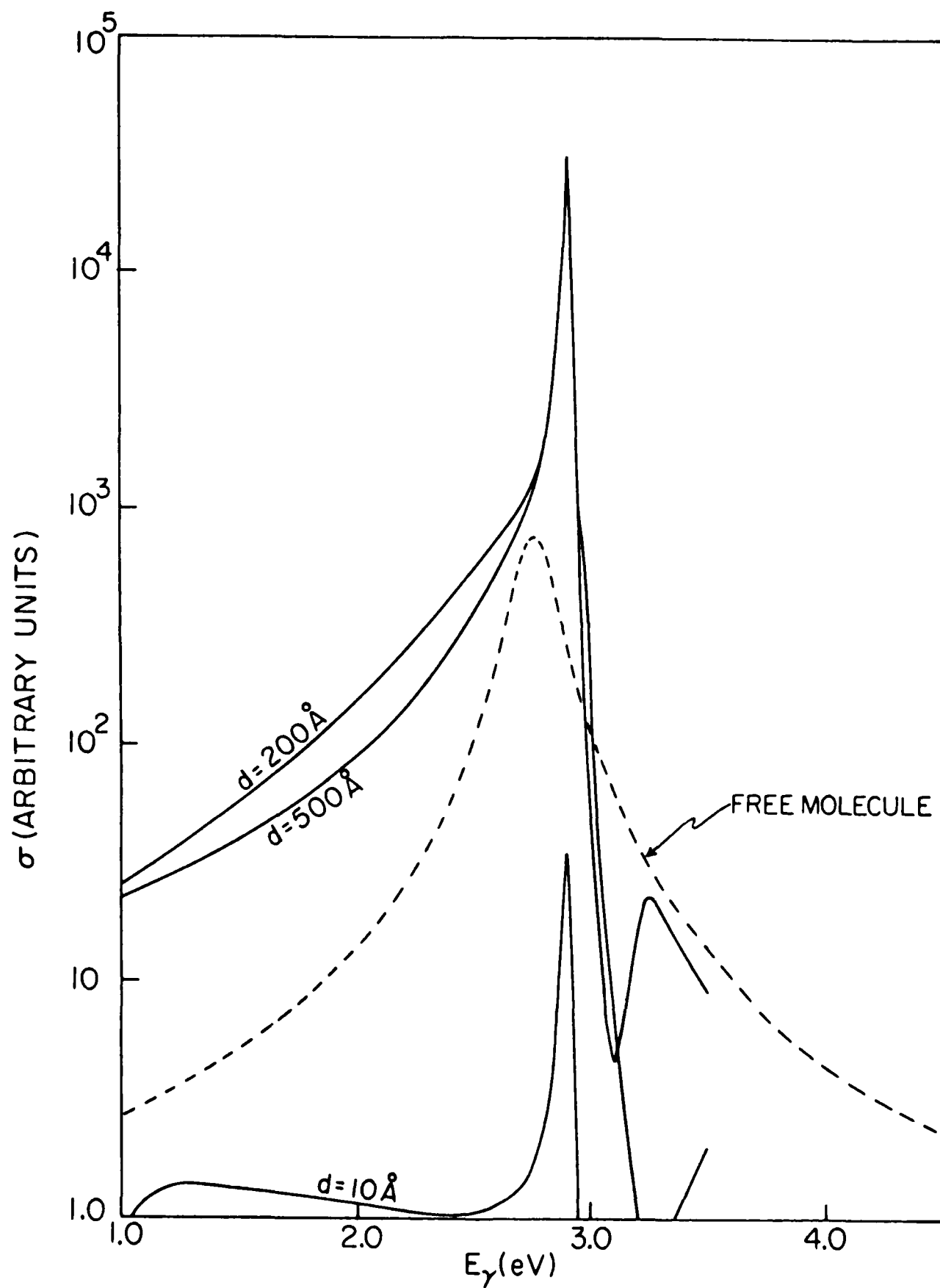
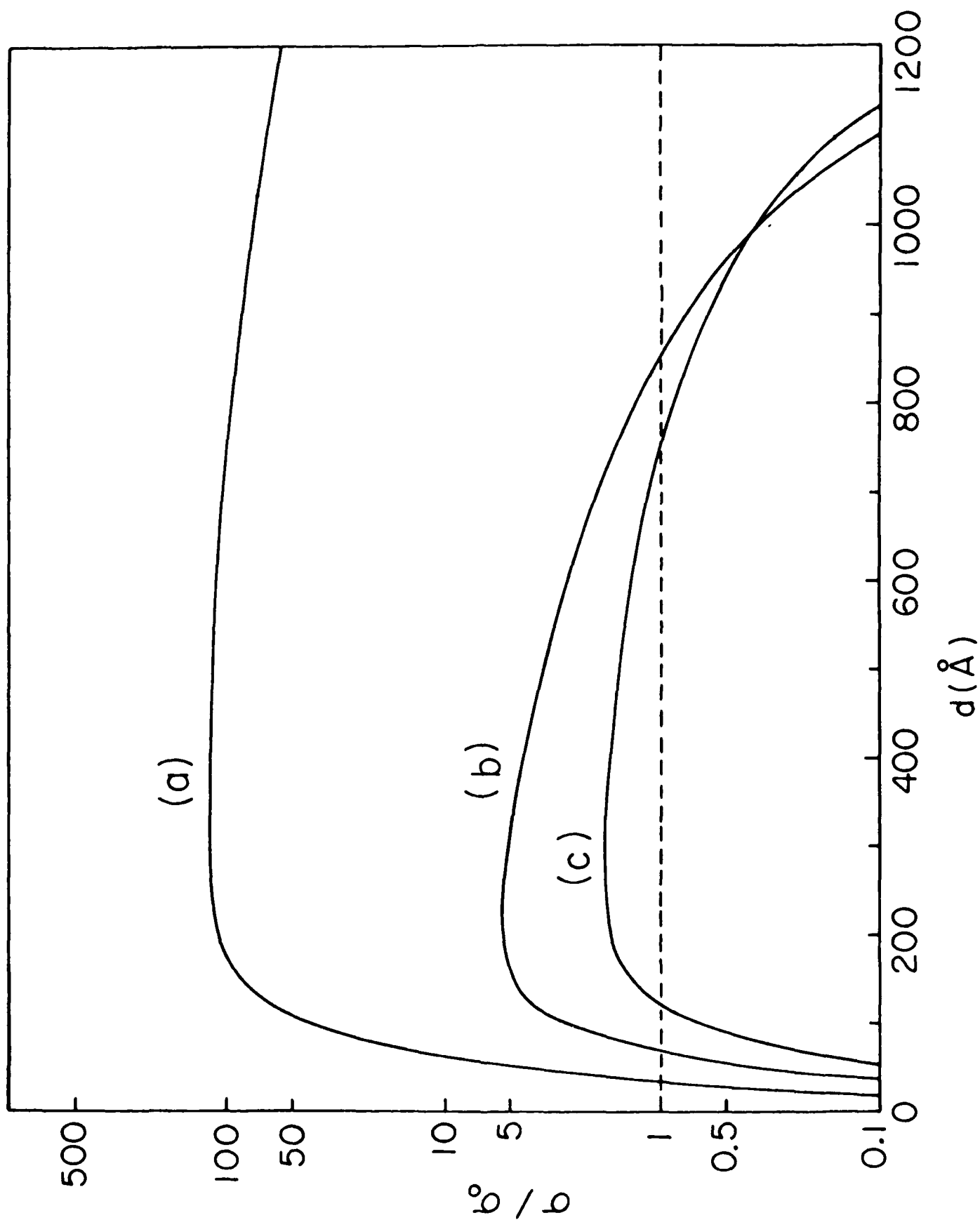


Figure 3



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